

## Association with poorly crystalline metal oxides: Effect on soil organic matter storage and stability in four eastern deciduous forest soils

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### Redox-active metals and the global carbon cycle

Strong association with mineral surfaces has been suggested as one mechanism underlying the long-term stabilization of organic matter in soils. Several recent studies have demonstrated a positive correlation between the content of poorly ordered crystalline metal oxide and hydroxide mineral phases and soil organic matter (SOM) or <sup>14</sup>C-based residence time. This positive correlation suggests that mineral-associated SOM persists over long time scales.

We utilized selective chemical dissolution (acid ammonium oxalate in the dark and sodium pyrophosphate) coupled with radiocarbon measurements to investigate the relationship between poorly crystalline Fe, Al, and Mn oxyhydroxide phases on organic matter storage and turnover time across four deciduous forest sites in the eastern U.S. comprising three different soil orders (inceptisol, spodosol alfisol).

Our results demonstrate that association with poorly-crystalline Fe and Al oxides (via adsorption to mineral surfaces and/or formation of soluble metal-OM complexes) do slow the turnover of SOM, with a significant positive linear relationship between radiocarbon turnover time and the content of oxalate extractable Al and Fe overall ( $R^2=0.60, P=0.0001, CL=95\%$ ). Piecewise regression analysis on turnover time vs. oxalate extractable metal oxide content for all four sites shows an apparent metal oxide threshold value at  $5\text{ g kg}^{-1}$ . Sites with oxalate extractable Fe and Al content below this value showed no statistically significant influence on SOM stability, presumably because the metal oxides are present in insufficient quantity to exert a measureable influence on the decomposability of SOM.

Soluble Fe and Al oxyhydroxide-OM complexes extracted via treatment with Na-pyrophosphate had a statistically significant influence on carbon storage at only one site (Bartlett Experimental Forest, spodosol) ( $R^2=0.92, P<0.0001, 95\%CL$ ). However a significant linear relationship between <sup>14</sup>C-based turnover time and Na-pyrophosphate extractable Fe and Al could not be demonstrated for any individual site. Thus, complexation of organic matter via reaction with Fe and Al oxide phases does not appear to be the dominant control on turnover time in the 0-15cm depth at the sites under study.

Harvard Forest (inceptisol) had the highest poorly crystalline Fe concentrations estimated as (oxalate extractable Fe) – (Na-pyrophosphate extractable Fe) and exhibited the strongest influence on <sup>14</sup>C based turnover times ( $R^2=0.82, P=0.0003, CL=95\%$ ); in this soil, poorly-crystalline Fe oxides and hydroxides are quantitatively important in stabilizing organic inputs against decomposition. Poorly crystalline Mn was found to exert a significant influence on SOM stability at a single site: Missouri Ozark Forest (alfisol) ( $R^2=0.65, P=0.0051, CL=95\%$ ). No significant effect for Mn on SOM storage could be demonstrated for any of the four sites under study.

## Analysis of oil inclusions by fs-laser ablation and ToF-SIMS

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### Femtosecond (fs) Laser Ablation

Recent advances in laser technology have led to ultrashort laser pulses capable of selectively opening and liberating oil within single inclusions. Coupling of an on-line femtosecond laser to a gas chromatograph-mass spectrometer successfully analysed hydrocarbon compounds from individual inclusions [1], but C<sub>19+</sub> compounds were undetected and potentially remained in the ablation chamber. To test this hypothesis, well characterized oils were ablated with an infrared (1030 nm) high repetition rate femtosecond laser and directly collected on filters placed at the exit of the ablation chamber. Analyses of filter extracts by GCxGC-ToF-MS showed the presence of unaltered C<sub>12+</sub> compounds including biomarkers. The success of the femtosecond laser as a sampling tool for biomarker analysis of oils was extended to the analysis of individual inclusions.

### Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

ToF-SIMS technology has been used to detect hopanes and steranes in single oil-bearing fluid inclusions [2]. Standard oil suites were used to calibrate the ToF-SIMS instrument for various hydrocarbon source rock facies allowing the determination of the origin of oils trapped in inclusions within the Elk Basin Field, Big Horn Basin, WY. The oils appear to be derived from a distal carbonate source (Phosphoria Formation) supporting long distance, lateral migration into the Big Horn Basin Fields from a mature Phosphoria source rock ~65-120Ma.

[1] Volk *et al.* (2010) *Organic Geochemistry* **41**, 74–77.

[2] Siljeström *et al.* (2010) *Geobiology* **8**, 37–44.